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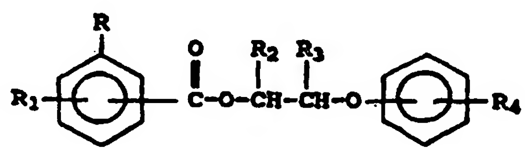
(71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).

(72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US).

(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).

(54) Title: AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS AND FUEL COMPOSITIONS CONTAINING THE SAME

(57) Abstract



(I)

Aromatic esters of polyalkylphenoxyalkanols having formula (I), or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1; R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000. The compounds of formula (I) are useful as fuel additives for the prevention and control of engine deposits.

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AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS AND FUEL COMPOSITIONS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to aromatic esters of polyalkylphenoxyalkanols and derivatives thereof. In a further aspect, this invention relates to the use of these compounds in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the

gasoline boiling range containing about 0.01 to 0.25 volume percent of a high molecular weight aliphatic hydrocarbon-substituted phenol in which the aliphatic hydrocarbon radical has an average molecular weight in the range of about 500 to 3,500. This patent teaches that gasoline compositions containing minor amounts of an aliphatic hydrocarbon-substituted phenol not only prevent or inhibit the formation of intake valve and port deposits in a gasoline engine, but also enhance the performance of the fuel composition in engines designed to operate at higher operating temperatures with a minimum of decomposition and deposit formation in the manifold of the engine.

Similarly, U.S. Patent No. 4,134,846, issued January 16, 1979 to Machleder et al., discloses a fuel additive composition comprising a mixture of (1) the reaction product of an aliphatic hydrocarbon-substituted phenol, epichlorohydrin and a primary or secondary mono- or polyamine, and (2) a polyalkylene phenol. This patent teaches that such compositions show excellent carburetor, induction system and combustion chamber detergency and, in addition, provide effective rust inhibition when used in hydrocarbon fuels at low concentrations.

Amino phenols are also known to function as detergents/dispersants, antioxidants and anti-corrosion agents when used in fuel compositions. U.S. Patent No. 4,320,021, issued March 16, 1982 to R. M. Lange, for example, discloses amino phenols having at least one substantially saturated hydrocarbon-based substituent of at least 30 carbon atoms. The amino phenols of this patent are taught to impart useful and desirable properties to oil-based lubricants and normally liquid fuels.

Similarly, U.S. Patent No. 3,149,933, issued September 22, 1964 to K. Ley et al., discloses hydrocarbon-substituted amino phenols as stabilizers for liquid fuels.

U.S. Patent No. 4,386,939, issued June 7, 1983 to R. M. Lange, discloses nitrogen-containing compositions prepared by reacting an amino phenol with at least one 3- or 4-membered ring heterocyclic compound in which the hetero atom is a single oxygen, sulfur or nitrogen atom, such as ethylene oxide. The nitrogen-containing compositions of this patent are taught to be useful as additives for lubricants and fuels.

Nitro phenols have also been employed as fuel additives. For example, U.S. Patent No. 4,347,148, issued August 31, 1982 to K. E. Davis, discloses nitro phenols containing at least one aliphatic substituent having at least about 40 carbon atoms. The nitro phenols of this patent are taught to be useful as detergents, dispersants, antioxidants and demulsifiers for lubricating oil and fuel compositions.

Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969 to M. Dubeck et al., discloses a liquid hydrocarbon fuel composition containing a major quantity of a liquid hydrocarbon of the gasoline boiling range and a minor amount sufficient to reduce exhaust emissions and engine deposits of an aromatic nitro compound having an alkyl, aryl, aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen substituent.

More recently, certain poly(oxyalkylene) esters have been shown to reduce engine deposits when used in fuel compositions. U.S. Patent No. 5,211,721, issued May 18, 1993 to R. L. Sung et al., for example, discloses an oil

soluble polyether additive comprising the reaction product of a polyether polyol with an acid represented by the formula RCOOH in which R is a hydrocarbyl radical having 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds of this patent are taught to be useful for inhibiting carbonaceous deposit formation, motor fuel hazing, and as ORI inhibitors when employed as soluble additives in motor fuel compositions.

Poly(oxyalkylene) esters of amino- and nitrobenzoic acids are also known in the art. For example, U.S. Patent No. 2,714,607, issued August 2, 1955 to M. Matter, discloses polyethoxy esters of aminobenzoic acids, nitrobenzoic acids and other isocyclic acids. These polyethoxy esters are taught to have excellent pharmacological properties and to be useful as anesthetics, spasmolytics, analeptics and bacteriostatics.

Similarly, U.S. Patent No. 5,090,914, issued February 25, 1992 to D. T. Reardan et al., discloses poly(oxyalkylene) aromatic compounds having an amino or hydrazinocarbonyl substituent on the aromatic moiety and an ester, amide, carbamate, urea or ether linking group between the aromatic moiety and the poly(oxyalkylene) moiety. These compounds are taught to be useful for modifying macromolecular species such as proteins and enzymes.

U.S. Patent No. 4,328,322, issued September 22, 1980 to R. C. Baron, discloses amino- and nitrobenzoate esters of oligomeric polyols, such as poly(ethylene) glycol. These materials are used in the production of synthetic polymers by reaction with a polyisocyanate.

U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz et al., discloses fuel compositions containing (1) one or more polybutyl or polyisobutyl alcohols wherein the polybutyl or polyisobutyl group has a number average molecular weight of 324 to 3,000, or (2) a poly(alkoxylate) of the polybutyl or polyisobutyl alcohol, or (3) a carboxylate ester of the polybutyl or polyisobutyl alcohol. This patent further teaches that when the fuel composition contains an ester of a polybutyl or polyisobutyl alcohol, the ester-forming acid group may be derived from saturated or unsaturated, aliphatic or aromatic, acyclic or cyclic mono- or polycarboxylic acids.

U.S. Patent Nos. 3,285,855, and 3,330,859 issued November 15, 1966 and July 11, 1967 respectively, to Dexter et al., disclose alkyl esters of dialkyl hydroxybenzoic and hydroxyphenylalkanoic acids wherein the ester moiety contains from 6 to 30 carbon atoms. These patents teach that such esters are useful for stabilizing polypropylene and other organic material normally subject to oxidative deterioration. Similar alkyl esters containing hindered dialkyl hydroxyphenyl groups are disclosed in U.S. Patent No. 5,196,565, which issued March 23, 1993 to Ross.

U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet et al., discloses alkyl esters of hydroxyphenyl carboxylic acids wherein the ester moiety may contain up to 23 carbon atoms. This patent teaches that such compounds are useful as antioxidants for stabilizing emulsion-polymerized polymers.

My prior U.S. Patent No. 5,407,452, issued April 18, 1995, and corresponding International Application Publication No. WO 95/04118, published February 9, 1995, disclose certain

poly(oxyalkylene) nitro and aminoaromatic esters having from 5 to 100 oxyalkylene units and teach the use of such compounds as fuel additives for the prevention and control of engine deposits.

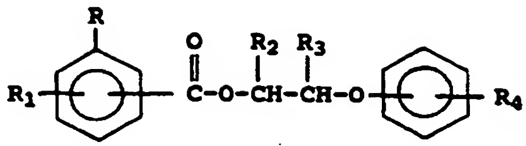
Similarly, my prior U.S. Patent No. 5,427,591, issued June 27, 1995, and corresponding International Application Publication No. WO 94/14926, published July 7, 1994, disclose certain poly(oxyalkylene) hydroxyaromatic esters which are useful as fuel additives to control engine deposits.

In addition, my prior U.S. Patent No. 5,380,345, issued January 10, 1995, and corresponding International Application Publication No. WO 95/15366, published June 8, 1995, disclose certain polyalkyl nitro and aminoaromatic esters useful as deposit control additives for fuels. Moreover, my prior International Application Publication No. WO 95/11955, published May 4, 1995, discloses certain polyalkyl hydroxyaromatic esters which are also useful as deposit control fuel additives.

SUMMARY OF THE INVENTION

I have now discovered certain aromatic esters of polyalkylphenoxyalkanols which provide excellent control of engine deposits, especially intake valve deposits, when employed as fuel additives in fuel compositions.

The compounds of the present invention include those having the following formula and fuel soluble salts thereof:



(I)

wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and a deposit-controlling effective amount of a compound of the present invention.

The present invention additionally provides a fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 150°F. to 400°F. and from about 10 to 70 weight percent of a compound of the present invention.

Among other factors, the present invention is based on the surprising discovery that certain aromatic esters of polyalkylphenoxyalkanols provide excellent control of engine deposits, especially on intake valves, when employed as additives in fuel compositions.

DETAILED DESCRIPTION OF THE INVENTION

Based on performance (e.g. deposit control), handling properties and performance/cost effectiveness, the preferred compounds of the invention are those wherein R is nitro, amino, N-alkylamino, or $—CH_2NH_2$ (aminomethyl). More preferably, R is a nitro, amino or $—CH_2NH_2$ group. Most preferably, R is an amino or $-CH_2NH_2$ group, especially amino. Preferably, R_1 is hydrogen, hydroxy, nitro or amino. More preferably, R_1 is hydrogen or hydroxy. Most preferably, R_1 is hydrogen. Preferably, R_4 is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000, more preferably about 700 to 3,000, and most preferably about 900 to 2,500. Preferably, the compound has a combination of preferred substituents.

Preferably, one of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen. More preferably, one of R_2 and R_3 is hydrogen, methyl or ethyl, and the other is hydrogen. Most preferably, R_2 is hydrogen, methyl or ethyl, and R_3 is hydrogen.

When R and/or R_1 is an *N*-alkylamino group, the alkyl group of the *N*-alkylamino moiety preferably contains 1 to 4 carbon atoms. More preferably, the *N*-alkylamino is *N*-methylamino or *N*-ethylamino.

Similarly, when R and/or R_1 is an *N,N*-dialkylamino group, each alkyl group of the *N,N*-dialkylamino moiety preferably contains 1 to 4 carbon atoms. More preferably, each alkyl group is either methyl or ethyl. For example, particularly preferred *N,N*-dialkylamino groups are *N,N*-dimethylamino, *N*-ethyl-*N*-methylamino and *N,N*-diethylamino groups.

A further preferred group of compounds are those wherein R is amino, nitro, or $-CH_2NH_2$ and R_1 is hydrogen or hydroxy. A particularly preferred group of compounds are those wherein R is amino, R_1, R_2 and R_3 are hydrogen, and R_4 is a polyalkyl group derived from polyisobutene.

It is preferred that the R substituent is located at the *meta* or, more preferably, the *para* position of the benzoic acid moiety, i.e., *para* or *meta* relative to the carbonyloxy group. When R_1 is a substituent other than hydrogen, it is particularly preferred that this R_1 group be in a *meta* or *para* position relative to the carbonyloxy group and in an *ortho* position relative to the R substituent. Further, in general, when R_1 is other than hydrogen, it is preferred that one of R or R_1 is located *para* to the carbonyloxy group and the other is located *meta* to the carbonyloxy group. Similarly, it is preferred that the R_4 substituent on the other phenyl ring is located *para* or *meta*, more preferably *para*, relative to the ether linking group.

The compounds of the present invention will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200°-250°C). Typically, the molecular weight of the compounds of this invention will range from about 700 to about 3,500, preferably from about 700 to about 2,500.

Fuel-soluble salts of the compounds of formula I can be readily prepared for those compounds containing an amino or substituted amino group and such salts are contemplated to be useful for preventing or controlling engine deposits. Suitable salts include, for example, those obtained by protonating the amino moiety with a strong organic acid,

such as an alkyl- or arylsulfonic acid. Preferred salts are derived from toluenesulfonic acid and methanesulfonic acid.

When the R or R_1 substituent is a hydroxy group, suitable salts can be obtained by deprotonation of the hydroxy group with a base. Such salts include salts of alkali metals, alkaline earth metals, ammonium and substituted ammonium salts. Preferred salts of hydroxy-substituted compounds include alkali metal, alkaline earth metal and substituted ammonium salts.

Definitions

As used herein, the following terms have the following meanings unless expressly stated to the contrary.

The term "amino" refers to the group: $-NH_2$.

The term "*N*-alkylamino" refers to the group: $-NHR_a$ wherein R_a is an alkyl group. The term "*N,N*-dialkylamino" refers to the group: $—NR_bR_c$, wherein R_b and R_c are alkyl groups.

The term "alkyl" refers to both straight- and branched-chain alkyl groups.

The term "lower alkyl" refers to alkyl groups having 1 to about 6 carbon atoms and includes primary, secondary and tertiary alkyl groups. Typical lower alkyl groups include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

The term "polyalkyl" refers to an alkyl group which is generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins,

such as ethylene, propylene, butylene, and the like. Preferably, the mono-olefin employed will have 2 to about 24 carbon atoms, and more preferably, about 3 to 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene, 1-octene and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, especially polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

The term "fuel" or "hydrocarbon fuel" refers to normally liquid hydrocarbons having boiling points in the range of gasoline and diesel fuels.

General Synthetic Procedures

The polyalkylphenoxyalkyl aromatic esters of this invention may be prepared by the following general methods and procedures. It should be appreciated that where typical or preferred process conditions (e.g., reaction temperatures, times, mole ratios of reactants, solvents, pressures, etc.) are given, other process conditions may also be used unless otherwise stated. Optimum reaction conditions may vary with the particular reactants or solvents used, but such conditions can be determined by one skilled in the art by routine optimization procedures.

Those skilled in the art will also recognize that it may be necessary to block or protect certain functional groups while conducting the following synthetic procedures. In such cases, the protecting group will serve to protect the functional group from undesired reactions or to block its undesired reaction with other functional groups or with the reagents used to carry out the desired chemical transformations. The proper choice of a protecting group

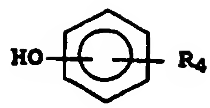
for a particular functional group will be readily apparent to one skilled in the art. Various protecting groups and their introduction and removal are described, for example, in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Second Edition, Wiley, New York, 1991, and references cited therein.

In the present synthetic procedures, a hydroxyl group will preferably be protected, when necessary, as the benzyl or tert-butyldimethylsilyl ether. Introduction and removal of these protecting groups is well described in the art. Amino groups may also require protection and this may be accomplished by employing a standard amino protecting group, such as a benzyloxycarbonyl or a trifluoroacetyl group. Additionally, as will be discussed in further detail hereinbelow, the aromatic esters of this invention having an amino group on the aromatic moiety will generally be prepared from the corresponding nitro derivative. accordingly, in many of the following procedures, a nitro group will serve as a protecting group for the amino moiety.

Moreover, the compounds of this invention having a $-CH_2NH_2$ group on the aromatic moiety will generally be prepared from the corresponding cyano derivative, -CN. Thus, in many of the following procedures, a cyano group will serve as a protecting group for the $-CH_2NH_2$ moiety.

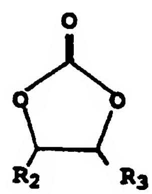
Synthesis

The polyalkylphenoxyalkyl aromatic esters of the present invention may be prepared by a process which initially involves hydroxyalkylation of a polyalkylphenol of the formula:



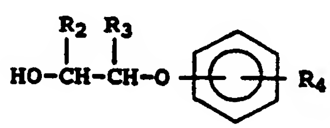
(II)

wherein R_4 is as defined herein, with an alkylene carbonate of the formula:



(III)

wherein R_2 and R_3 are as defined herein, in the presence of a catalytic amount of an alkali metal hydride or hydroxide, or alkali metal salt, to provide a polyalkylphenoxyalkanol of the formula:



(IV)

wherein R_2, R_3 and R_4 are as defined herein.

The polyalkylphenols of formula II are well known materials and are typically prepared by the alkylation of phenol with the desired polyolefin or chlorinated polyolefin. A further discussion of polyalkylphenols can be found, for example, in U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

Accordingly, the polyalkylphenols of formula II may be prepared from the corresponding olefins by conventional procedures. For example, the polyalkylphenols of formula II

above may be prepared by reacting the appropriate olefin or olefin mixture with phenol in the presence of an alkylating catalyst at a temperature of from about 25°C. to 150°C., and preferably 30°C. to 100°C. either neat or in an essentially inert solvent at atmospheric pressure. A preferred alkylating catalyst is boron trifluoride. Molar ratios of reactants may be used. Alternatively, molar excesses of phenol can be employed, i.e., 2 to 3 equivalents of phenol for each equivalent of olefin with unreacted phenol recycled. The latter process maximizes monoalkylphenol. Examples of inert solvents include heptane, benzene, toluene, chlorobenzene and 250 thinner which is a mixture of aromatics, paraffins and naphthenes.

The polyalkyl substituent on the polyalkylphenols employed in the invention is generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene, butylene, and the like. Preferably, the mono-olefin employed will have 2 to about 24 carbon atoms, and more preferably, about 3 to 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene, 1-octene and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, especially polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

The preferred polyisobutenes used to prepare the presently employed polyalkylphenols are polyisobutenes which comprise at least about 20% of the more reactive methylvinylidene isomer, preferably at least 50% and more preferably at least 70%. Suitable polyisobutenes include those prepared using BF_3 catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high

percentage of the total composition is described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes, known as "reactive" polyisobutenes, yield high molecular weight alcohols in which the hydroxyl group is at or near the end of the hydrocarbon chain. Examples of suitable polyisobutenes having a high alkylvinylidene content include Ultravis 30, a polyisobutene having a number average molecular weight of about 1300 and a methylvinylidene content of about 74%, and Ultravis 10, a polyisobutene having a number average molecular weight of about 950 and a methylvinylidene content of about 76%, both available from British Petroleum.

The alkylene carbonates of formula III are known compounds which are available commercially or can be readily prepared using conventional procedures. Suitable alkylene carbonates include ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, and the like. A preferred alkylene carbonate is ethylene carbonate.

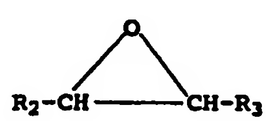
The catalyst employed in the reaction of the polyaklyphenol and alkylene carbonate may be any of the well known hydroxyalkylation catalysts. Typical hydroxyalkylation catalysts include alkali metal hydrides, such as lithium hydride, sodium hydride and potassium hydride, alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide, and alkali metal salts, for example, alkali metal halides, such as sodium chloride and potassium chloride, and alkali metal carbonates, such as sodium carbonate and potassium carbonate. The amount of catalyst employed will generally range from about 0.01 to 1.0 equivalent, preferably from about 0.05 to 0.3 equivalent.

The polyalkylphenol and alkylene carbonate are generally reacted in essentially equivalent amounts in the presence of the hydroxyalkylation catalyst at a temperature in the range of about 100°C. to 210°C., and preferably from about 150°C. to about 170°C. The reaction may take place in the presence or absence of an inert solvent.

The time of reaction will vary depending on the particular alkylphenol and alkylene carbonate reactants, the catalyst used and the reaction temperature. Generally, the reaction time will range from about two hours to about five hours. The progress of the reaction is typically monitored by the evolution of carbon dioxide. At the completion of the reaction, the polyalkylphenoxyalkanol product is isolated using conventional techniques.

The hydroxyalkylation reaction of phenols with alkylene carbonates is well known in the art and is described, for example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030 and 4,341,905.

Alternatively, the polyalkylphenoxyalkanol product of formula IV may be prepared by reacting the polyalkylphenol of formula II with an alkylene oxide of the formula:



(V)

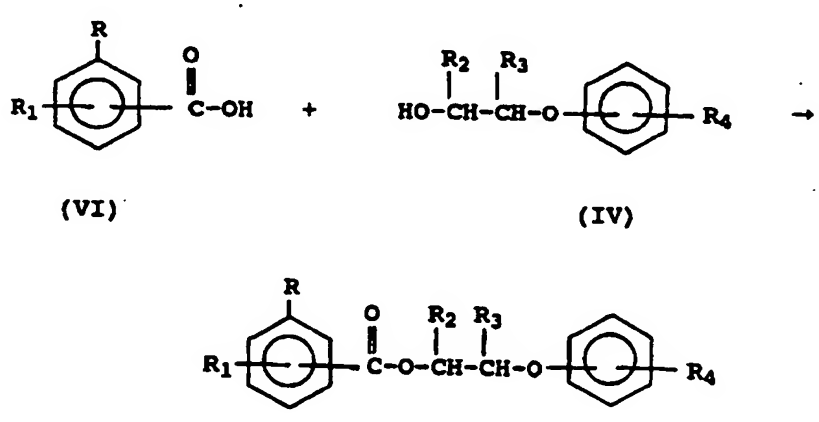
wherein R_2 and R_3 are as defined herein, in the presence of a hydroxyalkylation catalyst as described above.

Suitable alkylene oxides of formula V include ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene

oxide, and the like. A preferred alkylene oxide is ethylene oxide.

In a manner similar to the reaction with alkylene carbonate, the polyalkylphenol and alkylene oxide are reacted in essentially equivalent or equimolar amounts in the presence of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst, such as sodium or potassium hydride, at a temperature in the range of about 30°C. to about 150°C., for about 2 to about 24 hours. The reaction may be conducted in the presence or absence of a substantially anhydrous inert solvent. Suitable solvents include toluene, xylene, and the like. Generally, the reaction conducted at a pressure sufficient to contain the reactants and any solvent present, typically at atmospheric or higher pressure. Upon completion of the reaction, the polyalkylphenoxyalkanol is isolated by conventional procedures.

The polyalkylphenoxyalkanol of formula IV is subsequently reacted with a substituted benzoic acid of formula VI to provide the aromatic ester compounds of formula I. This reaction can be represented as follows:



(VI) (IV)

(I)

wherein R, R_1, R_2, R_3 and R_4 are as defined herein, and wherein any hydroxy or amino substituent on the substituted benzoic acid of formula VI is preferably protected with a suitable protecting group, for example, a benzyl or nitro group, respectively. Moreover, a $-CH_2NH_2$ substituent on the aromatic ring will preferably be protected by the use of a cyano group, CN.

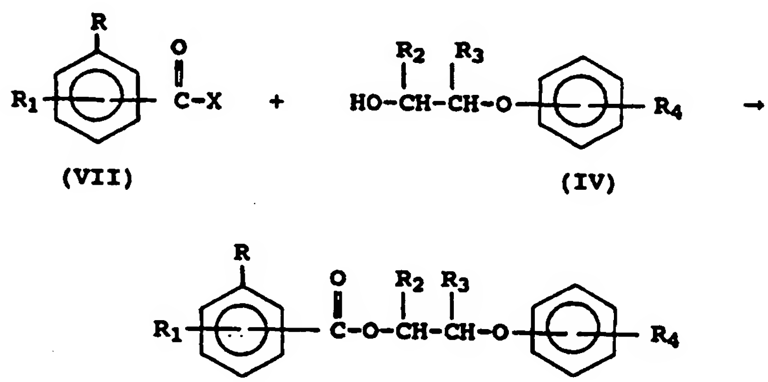
This reaction is typically conducted by contacting a polyalkylphenoxyalkanol of formula IV with about 0.25 to about 1.5 molar equivalents of the corresponding substituted and protected benzoic acid of formula VI in the presence of an acidic catalyst at a temperature in the range of about 70°C. to about 160°C. for about 0.5 to about 48 hours. Suitable acid catalysts for this reaction include p-toluene sulfonic acid, methanesulfonic acid and the like. Optionally, the reaction can be conducted in the presence of an inert solvent, such as benzene, toluene and the like. The water generated by this reaction is preferably removed during the course of the reaction, for example, by azeotropic distillation.

The substituted benzoic acids of formula VI are generally known compounds and can be prepared from known compounds using conventional procedures or obvious modifications thereof. Representative acids suitable for use as starting materials include, for example, 2-aminobenzoic acid (anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic acid, 3-amino-4-hydroxybenzoic acid, 4-amino-3-hydroxybenzoic acid, 2-nitrobenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic acid. When the R substituent is $-CH_2-NR_5R_6$, suitable

starting materials include 4-cyanobenzoic acid and 3-cyanobenzoic acid.

Preferred substituted benzoic acids include 3-nitrobenzoic acid, 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic acid, 3-cyanobenzoic acid and 4-cyanobenzoic acid.

The compounds formula I or their suitably protected analogs also can be prepared by reacting the polyalkylphenoxyalkanol of formula IV with an acid halide of the substituted benzoic acid of formula VI such as an acid chloride or acid bromide. This can be represented by the following reaction equation:


(VII) (IV) (I)

wherein X is halide, typically chloride or bromide, and R, R_1, R_2, R_3 and R_4 are as defined herein above, and wherein any hydroxy or amino substituents on the acid halide of formula VII are preferably protected with a suitable protection group, for example, benzyl or nitro, respectively. Also, when R is $-CH_2NR_5R_6$, a suitable starting material is a cyanobenzoyl halide.

Typically, this reaction is conducted by contacting the polyalkylphenoxyalkanol of formula IV with about 0.9 to about 1.5 molar equivalents of the acid halide of formula VII in an inert solvent, such as, for example, toluene, dichloromethane, diethyl ether, and the like, at a temperature in the range of about 25°C. to about 150°C. The reaction is generally complete in about 0.5 to about 48 hours. Preferably, the reaction is conducted in the presence of a sufficient amount of an amine capable of neutralizing the acid generated during the reaction, such as, for example, triethylamine, di(isopropyl)ethylamine, pyridine or 4-dimethylaminopyridine.

When the benzoic acids of formula VI or acid halides of formula VII contain a hydroxyl group, protection of the aromatic hydroxyl groups may be accomplished using well-known procedures. The choice of a suitable protecting group for a particular hydroxybenzoic carboxylic acid will be apparent to those skilled in the art. Various protecting groups, and their introduction and removal, are described, for example, in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Second Edition, Wiley, New York, 1991, and references cited therein.

After completion of the esterification, deprotection of the aromatic hydroxyl group can also be accomplished using conventional procedures. Appropriate conditions for this deprotection step will depend upon the protecting group(s) utilized in the synthesis and will be readily apparent to those skilled in the art. For example, benzyl protecting groups may be removed by hydrogenolysis under 1 to about 4 atmospheres of hydrogen in the presence of a catalyst, such as palladium on carbon. Typically, this deprotection reaction is conducted in an inert solvent, preferably a

mixture of ethyl acetate and acetic acid, at a temperature of from about 0°C. to about 40°C. for about 1 to about 24 hours.

When the benzoic acids of formula VI or acyl halides of formula VII have a free amino group ($-NH_2$) on the phenyl moiety, it is generally desirable to first prepare the corresponding nitro compound (i.e., where R and/or R_1 is a nitro group) using the above-described synthetic procedures, including preparation of the acyl halides, and then reduce the nitro group to an amino group using conventional procedures. Aromatic nitro groups may be reduced to amino groups using a number of procedures that are well known in the art. For example, aromatic nitro groups may be reduced under catalytic hydrogenation conditions; or by using a reducing metal, such as zinc, tin, iron and the like, in the presence of an acid, such as dilute hydrochloric acid. Generally, reduction of the nitro group by catalytic hydrogenation is preferred. Typically, this reaction is conducted using about 1 to 4 atmospheres of hydrogen and a platinum or palladium catalyst, such as palladium on carbon. The reaction is typically carried out at a temperature of about 0ºC. to about 100ºC. for about 1 to 24 hours in an inert solvent, such as ethanol, ethyl acetate and the like. Hydrogenation of aromatic nitro groups is discussed in further detail in, for example, P. N. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, pp. 113-137, Academic Press (1979); and *Organic Synthesis, Collective Vol. I*, Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941); and references cited therein.

Likewise, when the benzoic acids of formula VI or acyl halides of formula VII contain a $-CH_2NH_2$ group on the phenyl moiety, it is generally desirable to first prepare the

corresponding cyano compounds (i.e., where R and/or R_1 is a —CN group), and then reduce the cyano group to a —CH_2NH_2 group using conventional procedures. Aromatic cyano groups may be reduced to —CH_2NH_2 groups using procedures well known in the art. For example, aromatic cyano groups may be reduced under catalytic hydrogenation conditions similar to those described above for reduction of aromatic nitro groups to amino groups. Thus, this reaction is typically conducted using about 1 to 4 atmospheres of hydrogen and a platinum or palladium catalyst, such as palladium on carbon. Another suitable catalyst is a Lindlar catalyst, which is palladium on calcium carbonate. The hydrogenation may be carried out at temperatures of about 0°C. to about 100°C. for about 1 to 24 hours in an inert solvent such as ethanol, ethyl acetate, and the like. Hydrogenation of aromatic cyano groups is further discussed in the references cited above for reduction of aromatic nitro groups.

The acyl halides of formula VII can be prepared by contacting the corresponding benzoic acid compound of formula VI with an inorganic acid halide, such as thionyl chloride, phosphorous trichloride, phosphorous tribromide, or phosphorous pentachloride; or with oxalyl chloride. Typically, this reaction will be conducted using about 1 to 5 molar equivalents of the inorganic acid halide or oxalyl chloride, either neat or in an inert solvent, such as diethyl ether, at a temperature in the range of about 20°C. to about 80°C. for about 1 to about 48 hours. A catalyst, such as *N,N*-dimethylformamide, may also be used in this reaction. Again it is preferred to first protect any hydroxy or amino substituents before converting the benzoic acid to the acyl halide.

Fuel Compositions

The compounds of the present invention are useful as additives in hydrocarbon fuels to prevent and control engine deposits, particularly intake valve deposits. The proper concentration of additive necessary to achieve the desired deposit control varies depending upon the type of fuel employed, the type of engine, and the presence of other fuel additives.

In general, the concentration of the compounds of this invention in hydrocarbon fuel will range from about 50 to about 2500 parts per million (ppm) by weight, preferably from 75 to 1,000 ppm. When other deposit control additives are present, a lesser amount of the present additive may be used.

The compounds of the present invention may be formulated as a concentrate using an inert stable oleophilic (i.e., dissolves in gasoline) organic solvent boiling in the range of about 150°F. to 400°F. (about 65°C. to 205°C.). Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive will generally range from about 10 to about 70 weight percent, preferably 10 to 50 weight percent, more preferably from 20 to 40 weight percent.
In gasoline fuels, other fuel additives may be employed with the additives of the present invention, including, for example, oxygenates, such as t-butyl methyl ether, antiknock

agents, such as methylcyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, hydrocarbyl poly(oxyalkylene) aminocarbamates, or succinimides. Additionally, antioxidants, metal deactivators and demulsifiers may be present.

In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, and the like.

A fuel-soluble, nonvolatile carrier fluid or oil may also be used with the aromatic esters of this invention. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the nonvolatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, and synthetic polyoxyalkylene-derived oils, such as those described, for example, in U.S. Patent No. 4,191,537 to Lewis, and polyesters, such as those described, for example, in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to Vogel et al., and in European Patent Application Nos. 356,726, published March 7, 1990, and 382,159, published August 16, 1990.

These carrier fluids are believed to act as a carrier for the fuel additives of the present invention and to assist in removing and retarding deposits. The carrier fluid may also exhibit synergistic deposit control properties when used in

combination with a polyalkyl aromatic ester of this invention.

The carrier fluids are typically employed in amounts ranging from about 100 to about 5000 ppm by weight of the hydrocarbon fuel, preferably from 400 to 3000 ppm of the fuel. Preferably, the ratio of carrier fluid to deposit control additive will range from about 0.5:1 to about 10:1, more preferably from 1:1 to 4:1, most preferably about 2:1.

When employed in a fuel concentrate, carrier fluids will generally be present in amounts ranging from about 20 to about 60 weight percent, preferably from 30 to 50 weight percent.

PREPARATIONS AND EXAMPLES

A further understanding of the invention can be had in the following nonlimiting Examples. Wherein unless expressly stated to the contrary, all temperatures and temperature ranges refer to the Centigrade system and the term "ambient" or "room temperature" refers to about 20°C.-25°C. The term "percent" or "%" refers to weight percent and the term "mole" or "moles" refers to gram moles. The term "equivalent" refers to a quantity of reagent equal in moles, to the moles of the preceding or succeeding reactant recited in that example in terms of finite moles or finite weight or volume. Where given, proton-magnetic resonance spectrum (p.m.r. or n.m.r.) were determined at 300 mHz, signals are assigned as singlets (s), broad singlets (bs), doublets (d), double doublets (dd), triplets (t), double triplets (dt), quartets (q), and multiplets (m), and cps refers to cycles per second.

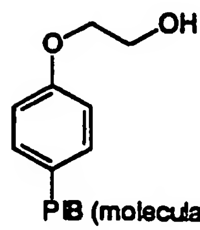
Example 1

Preparation of Polyisobutyl Phenol

To a flask equipped with a magnetic stirrer, reflux condenser, thermometer, addition funnel and nitrogen inlet was added 203.2 grams of phenol. The phenol was warmed to 40°C. and the heat source was removed. Then, 73.5 milliliters of boron trifluoride etherate was added dropwise. 1040 grams of Ultravis 10 Polyisobutene (molecular weight 950, 76% methylvinylidene, available from British Petroleum) was dissolved in 1,863 milliliters of hexane. The polyisobutene was added to the reaction at a rate to maintain the temperature between 22°C-27°C. The reaction mixture was stirred for 16 hours at room temperature. Then, 400 milliliters of concentrated ammonium hydroxide was added, followed by 2,000 milliliters of hexane. The reaction mixture was washed with water (3 X 2,000 milliliters), dried over magnesium sulfate, filtered and the solvents removed under vacuum to yield 1,056.5 grams of a crude reaction product. The crude reaction product was determined to contain 80% of the desired product by proton NMR and chromatography on silica gel eluting with hexane, followed by hexane: ethylacetate: ethanol (93:5:2).

Example 2

Preparation of

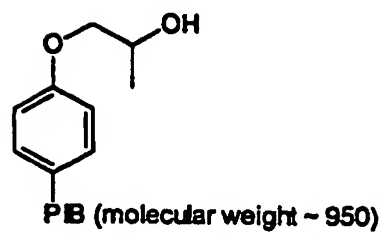


(molecular weight ~ 950)

1.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (99.7 grams, prepared as in Example 1) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Ethylene carbonate (8.6 grams) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and one milliliter of isopropanol was added. The reaction was diluted with one liter of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 98.0 grams of the desired product as a yellow oil.

Example 3

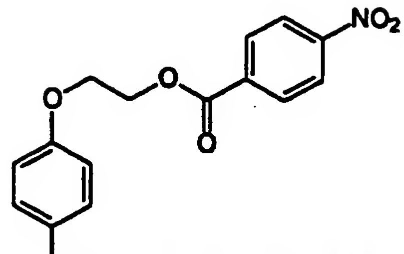
Preparation of



15.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 1301.7 grams of the desired product as a yellow oil.

Example 4

Preparation of

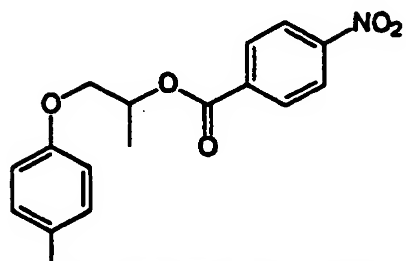


PIB (molecular weight ~ 950)

To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 2, 2.6 grams of 4-nitrobenzoic acid and 0.24 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 15.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (9:1) to afford 14.0 grams of the desired ester as a yellow oil. ^{1}H NMR ($CDCl_3$) d 8.3 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 4.7 (t, 2H), 4.3 (t, 2H), 0.7-1.6 (m, 137H).

Example 5

Preparation of

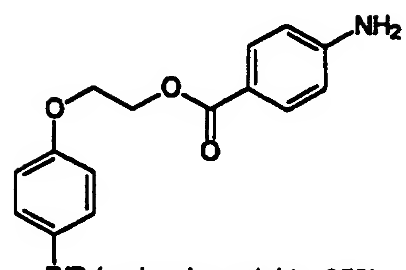


PB (molecular weight ~ 950)

To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 3, 2.7 grams of 4-nitrobenzoic acid and 0.23 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 16.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (8:2) to afford 15.2 grams of the desired ester as a brown oil. ^{1}H NMR ($CDCl_3$) d 8.2 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 5.55 (hx, 1H), 4.1 (t, 2H), 0.6-1.8 (m, 140H).

Example 6

Preparation of

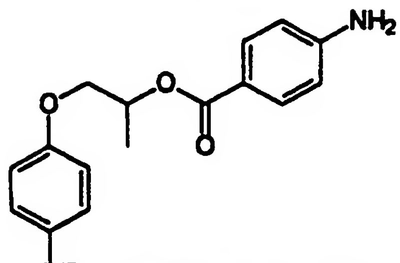


PIB (molecular weight ~ 950)

A solution of 9.4 grams of the product from Example 4 in 100 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yield 7.7 grams of the desired product as a yellow oil. ^{1}H NMR ($CDCl_3$) d 7.85 (d, 2H), 7.3 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 4.6 (t, 2H), 4.25 (t, 2H), 4.05 (bs, 2H), 0.7-1.6 (m, 137H).

Example 7

Preparation of



PIB (molecular weight ~ 950)

A solution of 15.2 grams of the product from Example 5 in 200 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yield 15.0 grams of the desired product as a brown oil. ^{1}H NMR ($CDCl_3/D_2O$) d 7.85 (d, 2H), 7.25 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 5.4 (hx, 1H), 3.8-4.2 (m, 4H), 0.6-1.8 (m, 140H).

Example 8

Single-Cylinder Engine Test

The test compounds were blended in gasoline and their deposit reducing capacity determined in an ASTM/CFR single-cylinder engine test.

A Waukesha CFR single-cylinder engine was used. Each run was carried out for 15 hours, at the end of which time the intake valve was removed, washed with hexane and weighed. The previously determined weight of the clean valve was

subtracted from the weight of the value at the end of the run. The differences between the two weights is the weight of the deposit. A lesser amount of deposit indicates a superior additive. The operating conditions of the test were as follows: water jacket temperature 200°F; vacuum of 12 in Hg, air-fuel ratio of 12, ignition spark timing of 400 BTC; engine speed is 1800 rpm; the crankcase oil is a commercial 30W oil.

The amount of carbonaceous deposit in milligrams on the intake valves is reported for each of the test compounds in Table I.

TABLE I

Sample[1]	Intake Valve Deposit Weight (in milligrams) Run 1	Run 2	Average
Base Fuel	354.9	333.5	344.2
Example 4	169.0	178.0	173.5
Example 6	13.4	12.2	12.8

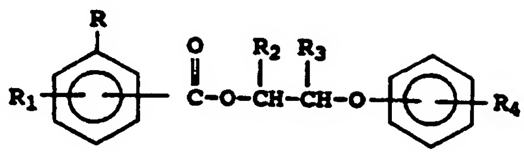
[1]At 150 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 150 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the aromatic esters of polyalkylphenoxyalkanols of the present invention (Examples 4 and 6) compared to the base fuel.

WHAT IS CLAIMED IS:

1. A compound of the formula:



or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

2. The compound according to Claim 1, wherein R is nitro, amino or $-CH_2NH_2$.

3. The compound according to Claim 2, wherein R is amino, or $-CH_2NH_2$.

4. The compound according to Claim 3, wherein R is amino.

5. The compound according to Claim 1, wherein R_1 is hydrogen, hydroxy, nitro or amino.

6. The compound according to Claim 5, wherein R_1 is hydrogen or hydroxy.

7. The compound according to Claim 6, wherein R_1 is hydrogen.

8. The compound according to Claim 1, wherein one of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen.

9. The compound according to Claim 8, wherein one of R_2 and R_3 is hydrogen, methyl or ethyl, and the other is hydrogen.

10. The compound according to Claim 9, wherein R_2 is hydrogen, methyl or ethyl, and R_3 is hydrogen.

11. The compound according to Claim 1, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000.

12. The compound according to Claim 11, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 700 to 3,000.

13. The compound according to Claim 12, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 900 to 2,500.

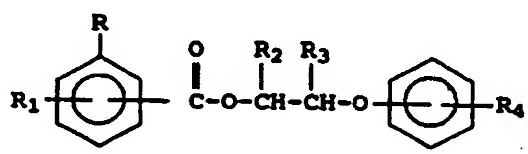
14. The compound according to Claim 1, wherein R_4 is a polyalkyl group derived from polypropylene, polybutene, or a polyalphaolefin oligomer of 1-octene or 1-decene.

15. The compound according to Claim 14, wherein R_4 is a polyalkyl group derived from polyisobutene.

16. The compound according to Claim 15, wherein the polyisobutene contains at least about 20% of a methylvinylidene isomer.

17. The compound according to Claim 1, wherein R is amino, R_1, R_2 and R_3 are hydrogen and R_4 is a polyalkyl group derived from polyisobutene.

18. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a compound of the formula:



or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

19. The fuel composition according to Claim 18, wherein R is nitro, amino or $-CH_2NH_2$.

20. The fuel composition according to Claim 19, wherein R is amino, or $-CH_2NH_2$.

21. The fuel composition according to Claim 20, wherein R is amino.

22. The fuel composition according to Claim 18, wherein R_1 is hydrogen, hydroxy, nitro or amino.

23. The fuel composition according to Claim 22, wherein R_1 is hydrogen or hydroxy.

24. The fuel composition according to Claim 23, wherein R_1 is hydrogen.

25. The fuel composition according to Claim 18, wherein one of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen.

26. The fuel composition according to Claim 25, wherein one of R_2 and R_3 is hydrogen, methyl or ethyl, and the other is hydrogen.

27. The fuel composition according to Claim 26, wherein R_2 is hydrogen, methyl or ethyl, and R_3 is hydrogen.

28. The fuel composition according to Claim 18, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000.

29. The fuel composition according to Claim 28, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 700 to 3,000.

30. The fuel composition according to Claim 29, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 900 to 2,500.

31. The fuel composition according to Claim 18, wherein R_4 is a polyalkyl group derived from polypropylene, polybutene, or a polyalphaolefin oligomer of 1-octene or 1-decene.

32. The fuel composition according to Claim 31, wherein R_4 is a polyalkyl group derived from polyisobutene.

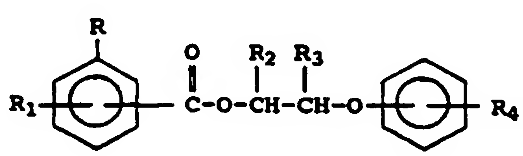
33. The fuel composition according to Claim 32, wherein the polyisobutene contains at least about 20% of a methylvinylidene isomer.

34. The fuel composition according to Claim 18, wherein R is amino, R_1, R_2 and R_3 are hydrogen and R_4 is a polyalkyl group derived from polyisobutene.

35. The fuel composition according to Claim 18, wherein the composition contains from about 50 to about 2,000 parts per million by weight of said compound.

36. The fuel composition according to Claim 18, where the composition further contains from about 100 to about 5,000 parts per million by weight of a fuel-soluble, nonvolatile carrier fluid.

37. A fuel concentrate comprising an inert stable oleophilic organic solvent boiling in the range of from about 150°F. to 400°F. and from about 10 to about 70 weight percent of a compound of the formula:



or a fuel soluble salt thereof, wherein R is hydroxy, nitro or $-(CH_2)_x-NR_5R_6$, wherein R_5 and R_6 are

independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

R_1 is hydrogen, hydroxy, nitro or $-NR_7R_8$, wherein R_7 and R_8 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_2 and R_3 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

R_4 is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

38. The fuel concentrate according to Claim 37, wherein R is nitro, amino or $-CH_2NH_2$.

39. The fuel concentrate according to Claim 38, wherein R is amino, or $-CH_2NH_2$.

40. The fuel concentrate according to Claim 39, wherein R is amino.

41. The fuel concentrate according to Claim 37, wherein R_1 is hydrogen, hydroxy, nitro or amino.

42. The fuel concentrate according to Claim 41, wherein R_1 is hydrogen or hydroxy.

43. The fuel concentrate according to Claim 42, wherein R_1 is hydrogen.

44. The fuel concentrate according to Claim 37, wherein one of R_2 and R_3 is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen.

45. The fuel concentrate according to Claim 44, wherein one of R_2 and R_3 is hydrogen, methyl or ethyl, and the other is hydrogen.

46. The fuel concentrate according to Claim 45, wherein R_2 is hydrogen, methyl or ethyl, and R_3 is hydrogen.

47. The fuel concentrate according to Claim 37, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000.

48. The fuel concentrate according to Claim 47, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 700 to 3,000.

49. The fuel concentrate according to Claim 48, wherein R_4 is a polyalkyl group having an average molecular weight in the range of about 900 to 2,500.

50. The fuel concentrate according to Claim 37, wherein R_4 is a polyalkyl group derived from polypropylene, polybutene, or a polyalphaolefin oligomer of 1-octene or 1-decene.

51. The fuel concentrate according to Claim 50, wherein R_4 is a polyalkyl group derived from polyisobutene.

52. The fuel concentrate according to Claim 51, wherein the polyisobutene contains at least about 20% of a methylvinylidene isomer.

53. The fuel concentrate according to Claim 37, wherein R is amino, R_1, R_2 and R_3 are hydrogen and R_4 is a polyalkyl group derived from polyisobutene.

54. The fuel concentrate according to Claim 37, wherein the fuel concentrate further contains from about 20 to about 60 weight percent of a fuel-soluble, nonvolatile carrier fluid.